FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	ATTORNEY'S DOCKET NUMBER: BO 42433 JGD U.S. APPLN. NO. (If known, see 37 CFR 1.5) 10/019492

INTERNATIONAL APPLICATION NO.: PCT/NL00/00462	INTERNATIONAL FILING DATE: 30 JUNE 2000 (30.06.00)	PRIORITY DATE CLAIMED: 30 JUNE 1999 (30.06.99)

TITLE OF INVENTION: BLEACH ACTIVATOR BASED ON INULIN

APPLICANT(S) FOR DO/EO/US: Mariëtte Ellen Boukje BOLKENBAAS, Henricus Wilhelmus Carolina RAAIJMAKERS, Hendrika Cornelia KUZEE, Henkrik Arend VAN DOREN and Ingrid Karin HAAKSMAN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Item 11. to 16. below concern document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A **FIRST** preliminary amendment.
    [ ] A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information: INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT/IPEA/409), INTERNATIONAL SEARCH REPORT (PCT/ISA/210), APPLICATION DATA SHEET, ABSTRACT

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NO.
10/019492	PCT/NL00/00462	BO 42433 JGD

	CALCULATIONS PTO USE ONLY

17. [X] The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR1.482) nor international search fee (37 CFR1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... $ 1,040.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... $ 890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... $ 740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... $ 710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... $ 100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 890.00
Surcharge of $130.00 for furnishing the oath or declaration later than 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$
Total claims	20 - 20 =	0	X $18.00	$
Independent claims	3 - 3 =	0	X $84.00	$
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+ $280.00	$
TOTAL OF ABOVE CALCULATIONS =				$ 890.00
Reduction of ½ for filing by small entity, if applicable. Applicant claims Small Entity Status under 37 CFR 1.27. +				$
SUBTOTAL =				$ 890.00
Processing fee of $130 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR1.492(f)).				$
TOTAL NATIONAL FEE =				$ 890.00
Fee for recording the enclosed assignment (37 CFR1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$ 40.00
TOTAL FEES ENCLOSED =				$ 930.00
				Amount to be refunded:
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a. [X] A check in the amount of $ **930.00** to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. **25-0120** in the amount of $ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required by 37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. **25-0120**. A duplicate copy of this sheet is enclosed.

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December 31, 2001

By _____
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PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Mariëtte BOLKENBAAS et al.

Serial No. (unknown)

Filed herewith

BLEACH ACTIVATOR BASED ON INULIN

PRELIMINARY AMENDMENT

Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to the first Official Action and calculation of the filing fee, please substitute Claims 1-10 as originally filed, which appear on page 9, with Claims 1-10 as filed in the Article 34 amendment of June 26, 2001. The page containing Claims 1-10 is marked "AMENDED SHEET" and is attached hereto. Following the insertion of Claims 1-10, please amend these claims as follows:

IN THE CLAIMS:

Please amend claims 1-7 and 10 as follows:

--1.(Amended) A method of activating bleach comprising the step of combining with the bleach a partially acylated fructan having a degree of substitution with acyl groups of 0.4-2.5 and a degree of substitution of less than 0.5 with other substituents.

2.(Amended) The method according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

3.(Amended) The method according to Claim 1, wherein the fructan is acylated with a degree of substitution of 0.6-1.8.

4.(Amended) The method according to Claim 1, wherein the fructan has an average chain length of 3-60, in particular 4-30.

5.(Amended) The method according to Claim 1, wherein the degree of substitution of carboxymethyl groups is less than 0.2.

6.(Amended) The method according to Claim 1, wherein the fructan is inulin.

7.(Amended) The method according to Claim 1, wherein the fructan is acylated with at least one of acetyl and/or propionyl groups.

10.(Amended) Partially acetylated and/or propionylated fructan produced by acylation of the fructan or derivative thereof with a reactive acyl derivative of a acetic and/or propionic acid, characterised in that the acylation is carried out in an aqueous medium at a pH of between 7 and 9, wherein the fructan has solubility in water of at least 1 g/l.--

IN THE ABSTRACT:

Please delete the abstract as originally filed which appears on the cover sheet of the Published Application. Add new abstract as enclosed herewith on a separate sheet.

ADD NEW CLAIMS 11-20:

--11.(New) The method according to Claim 2, wherein the fructan is acylated with a degree of substitution of 0.6-1.8.--

--12.(New) The method according to Claim 2, wherein the fructan has an average chain length of 3-60, in particular 4-30.--

--13.(New) The method according to Claim 3, wherein the fructan has an average chain length of 3-60, in particular 4-30.--

--14.(New) The method according to Claim 2, wherein the degree of substitution of carboxymethyl groups is less than 0.2.--

--15.(New) The method according to Claim 3, wherein the degree of substitution of carboxymethyl groups is less than 0.2.--

--16. (New) The method according to Claim 4, wherein the degree of substitution of carboxymethyl groups is less than 0.2.--

--17. (New) The method according to Claim 2, wherein the fructan is inulin.--

--18. (New) The method according to Claim 3, wherein the fructan is inulin.--

--19. (New) The method according to Claim 4, wherein the fructan is inulin.--

--20. (New) The fructan of claim 10, having a solubility in water of at least 2 g/l.--

R E M A R K S

The above changes in the claims merely place this national phase application in the same condition as it was during Chapter II of the international phase, with the multiple dependencies being removed. Following entry of this amendment by substitution of the pages, only claims 1-20

remain pending in this application. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned **"VERSION WITH MARKINGS TO SHOW CHANGES MADE"**.

Respectfully submitted,

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December 31, 2001

"VERSION WITH MARKINGS TO SHOW CHANGES MADE"

Claims 1-7 and 10 have been amended as follows:

~~1. Use of~~1. (Amended) A method of activating bleach ~~comprising the step of combining with the bleach~~ a partially acylated fructan having a degree of substitution with acyl groups of 0.4-2.5 and a degree of substitution of less than 0.5 with other substituents ~~as a bleach activator~~.

~~2. Use~~2. (Amended) ~~The method~~ according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

~~3. Use~~3. (Amended) ~~The method~~ according to Claim 1 ~~or 2~~, wherein the fructan is acylated with a degree of substitution of 0.6-1.8.

~~4. Use~~4. (Amended) ~~The method~~ according to ~~one of Claims 1-3,~~ ~~Claim 1,~~ wherein the fructan has an average chain length of 3-60, in particular 4-30.

~~5. Use~~5. (Amended) ~~The method~~ according to ~~one of Claims 1-4,~~ ~~Claim 1,~~ wherein the degree of substitution of carboxymethyl groups is less than 0.2.

~~6. Use~~6. (Amended) ~~The method~~ according to ~~one of Claims 1-5,~~ ~~Claim 1,~~ wherein the fructan is inulin.

~~7. Use~~7. (Amended) ~~The method~~ according to ~~one of Claims 1-6,~~ ~~Claim 1,~~ wherein the fructan is acylated with at least one of acetyl and/or propionyl groups.

10. (Amended) Partially acetylated and/or propionylated fructan produced by acylation of the fructan or derivative thereof with a reactive acyl derivative of a acetic and/or propionic acid, characterised in that the ~~obtainable using the method according to Claim 8 or 9, which~~acylation is carried out in an aqueous medium at a pH of between 7 and 9, wherein the fructan has solubility in water of at least 1~~g/l, in particular of at least 2~~ g/l.

Claims

1. Use of a partially acylated fructan having a degree of substitution with acyl groups of 0.4 - 2.5 and a degree of substitution of less than 0.5 with other substituents as a bleach activator.

2. Use according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

3. Use according to Claim 1 or 2, wherein the fructan is acylated with a degree of substitution of 0.6 - 1.8.

4. Use according to one of Claims 1 - 3, wherein the fructan has an average chain length of 3 - 60, in particular 4 - 30.

5. Use according to one of Claims 1 - 4, wherein the degree of substitution of carboxymethyl groups is less than 0.2.

6. Use according to one of Claims 1 - 5, wherein the fructan is inulin.

7. Use according to one of Claims 1 - 6, wherein the fructan is acylated with acetyl and/or propionyl groups.

8. A process of producing an acetylated and/or propionylated fructan or fructan derivative by acylation of the fructan or derivative thereof with a reactive acyl derivative of acetic and/or propionic acid, characterised in that the acylation is carried out in an aqueous medium at a pH of between 7 and 9.

9. A process according to Claim 8, characterised in that the acylation is carried out at a temperature of between 0 and 40 °C.

10. Partially acetylated and/or propionylated fructan obtainable using the method according to Claim 8 or 9, which has a solubility in water of at least 1 g/l, in particular of at least 2 g/l.

1/pats

Bleach activator based on inulin

The invention relates to the use of fructan derivatives as a bleach activator.

In addition to a bleaching agent, such as a peroxide, percarbonate or perborate, a bleach activator is usually needed for bleaching, for example, textile materials in the washing process. The most widely used bleach activator is tetraacetylethylenediamine (TAED). The disadvantage of TAED is that it is moderately to poorly biodegradable and is thus an undesired constituent in waste water. The use of acetylated sucrose (degree of substitution 4.5 - 7), in particular hexa-acetylsucrose, as bleach activator is disclosed in EP-A 492 000. Peracetylated sugar acids (sucrose, maltose, lactose) having a bleach-activating action are disclosed in EP-A 731 161. Acetylated carboxymethylinulin derivatives which are said to have a bleach-activating action are described in EP-A 814 088.

It has been found that acylated fructans and fructan derivatives are outstandingly suitable as a bleach activator, having an activity comparable to that of TAED and having much better biodegradability. The acylated fructans and fructan derivatives to be used according to the invention have an average degree of substitution (in acyl groups) of 0.4 - 2.5, preferably of 0.6 - 1.8 and preferentially of 0.8 - 1.6. Surprisingly the bleach-activating action of the acylated inulins according to the invention is also found to be better than that of the comparable acylated carboxymethylinulins according to EP-A 814 088. The acyl groups in the acylated fructan according to the invention are preferably derived from monocarboxylic acids and can be acetyl, propionyl, butyryl and higher alkanoyl groups (for example up to C12, in particular up to C6) and optionally formyl, alkenoyl, pyruvyl and benzoyl groups and the like, including mixtures, for example of acetyl and propionyl groups, both within a molecule (acetylpropionylfructan) and of different substances (acetylfructan and propionylfructan), as long as the total or average degree of substitution is within the set limits.

Acylated inulin is known per se from EP-A 792 888. The acylated inulins described in this publication preferably have a degree of substitution of 0.5 or less and are proposed as a surfactant.

Here fructans are understood to be all oligosaccharides and polysaccharides which have a majority of anhydrofructose units. The fructans can have a polydisperse chain length distribution and can be straight-chain or branched. The fructans comprise both products obtainable directly from a vegetable or other source and the products in which the average

chain length has been modified (increased or reduced) by fractionation, enzymatic hydrolysis or synthesis. The fructans have an average chain length (= degree of polymerisation, DP) of at least 3, up to about 1000, in particular of 3 to 60 monosaccharide units. Preferably the fructan contains mainly β-2,1 bonds, as in inulin. Inulin can be obtained, inter alia, from chicory, dahlias and Jerusalem artichokes.

Acylated reduced fructans can also be used. Reduced fructans are fructans in which reducing end groups (usually fructose groups) have been reduced, for example using sodium borohydride or using hydrogen in the presence of a transition metal catalyst.

Furthermore, chemically or physically modified fructans can serve as the basis for acylated derivatives. The chemical modification preferably corresponds to a degree of substitution in the modification of less than 0.5, in particular less than 0.2. The modification can be, for example, an alkyl group, hydroxyalkyl group, carboxyalkyl group, alkoxy-carbonylalkyl group, carboxyl group, alkoxycarbonyl group, aminoalkyl group or acylamino group.

Various methods of preparation for acylated fructans and fructan derivatives are available. Reaction of carboxymethylinulin (DS 1.0) with excess acetic anhydride in the presence of sodium acetate at 120 °C (analogous to Example 12 in EP 792 888) yields a product which has a relatively low content of acetyl groups (DS acetyl = 0.78). Virtually complete acetylation in good yield (89%) can be achieved by carrying out this reaction at 140 °C (analogous to the R.L. Whistler method, *Methods in Carbohydrate Chemistry,* Vol II, 211-212).

It has been found that the reaction of fructans and fructan derivatives with acetic anhydride in water at controlled pH is an exceptionally suitable method for the preparation of partially acylated fructans and fructan derivatives. The pH is kept constant at a value of between 7 and 9, preferably of about 8, during the reaction. The reaction temperature is between 0 and 80 °C, preferably between 0 and 40 °C. This method results in the formation of partially acylated fructans and fructan derivatives in good yield (85 - 95%) and with a high reaction efficiency (50 - 75%); the reaction efficiency is defined as the degree of acylation determined divided by the maximum degree of acylation calculated on the basis of the quantity of acylating agent (DS_{det}/DS_{theor} x 100%). Instead of acid anhydrides it is also possible to use other reactive acyl derivatives, such as acid halides, reactive esters, in particular vinyl esters, such as vinyl acetate and vinyl propionate, for the acylation.

It has been found that the partial acetylation of carboxymethylinulin (CMI) in a mixture of acetic acid, acetic anhydride and sulphuric acid analogous to EP 814 088 leads only to a product in low yield (41%) and with a low reaction efficiency (8%).

The bleach activator property is determined on the basis of the quantity of peracetic acid that can be liberated from the product. It has been found that the bleach activator properties of the (partially) acylated fructans and fructan derivatives depend on the method by which the acylation has been carried out. The best characteristics are found when the acylation is carried out in water at controlled pH (Table 1).

The acetylation of CMI with acetic anhydride, acetic acid and sulphuric acid (EP 814 088) or acetic anhydride and sodium acetate at elevated temperature yields products which have poor solubility in water and low activity as bleach activator.

Partial acylation of CMI by reaction of CMI with acetic anhydride in water at controlled pH gives products which have adequate solubility in water and better results in the bleach activator test. The solubility in water is appreciably higher than that of corresponding products prepared in accordance with the prior art. The invention also relates to such an acylation method and to the products having a solubility in water of at least 1g/l which are obtainable in this way.

Surprisingly it has been found that the lower the degree of substitution of carboxymethyl groups in partially acetylated CMI the better is the action as bleach activator. Preferably partially acetylated CMI having a degree of substitution of carboxymethyl groups of less than 0.2 is used.

For partially acetylated inulin (no carboxyl groups present) it is found that the solubility of the products obtained is good up to a DS_{acetyl} of 2.0. The bleach activator action of these compounds is better than that of partially acetylated CMI. The action of partially acetylated inulin having a DS of 1.7 approaches the action of TAED and SORMAN. A possible explanation for these results is that the bleach activator action appears to be determined by the solubility in water and the availability of the acetyl groups. The mol % peracetate formed is a measure of the availability of the acetyl groups. Poor solubility in water gives low availability of the acetyl groups for peracetate formation.

Table 1: Solubility and bleach activator action of partially acetylated CMI, partially acetylated inulin, SORMAN and TAED on the basis of amount of peracetate liberated

DS (carboxymethyl)	DS (acetyl)	Synthesis method[1]	Solubility (%)	Peracetate formed (mol%)[2]	mol peracetate/ kg product
1	0.51	A	<0.1	39	0.8
1	1.05	B	<0.1	17	0.5
1	1.5	C	<0.1	20	1.0
0.2	0.66	D	>5	67	2.1
0.85	0.73	D	>5	51	1.4
1.5	1.12	D	>5	16	0.5
0	0.58	D	>5	73	2.3
0	1.01	D	>5	74	3.7
0	1.53	D	>5	73	5.0
0	1.71	D	>5	71	5.2
0	3.0	C	<0.1	4	0.1
0	0	-	10	-	-
1	0	-	50	-	-
Comparison:					
TAED[3]	4.0	-	0.1	45	7.9
SORMAN[4]	6.0	-	0.1	44	6.0

1: A: AcOH/Ac_2O/H_2SO_4, 50 °C, 3 hours; B: Ac_2O/NaOAc, 120 °C, 4 hours; C: Ac_2O/NaOAc, 140 °C, 4 hours; D: Ac_2O/H_2O, pH 8, 25 °C.

2: 100 x number of mols of peracetate formed / total number of mols of acetyl groups in product.

3: tetraacetylethylenediamine

4: mixture of peracetylsorbitol and peracetylmannitol (EP 525 239)

It can clearly be seen from Table 1 that the presence of carboxyl groups in the inulin molecule has an adverse effect on the availability of the acetyl groups for peracetate formation. The quantity of peracetate/kg product is also adversely affected as a result.

For partially acetylated inulin the availability of the acetyl groups is virtually independent of the degree of acetylation to a maximum DS of approximately 2. This means that the quantity of peracetate per kg product increases virtually in proportion with the degree of substitution (Figure 1). Above DS 2 the solubility, and thus also the availability of acetyl groups for peracetate formation, decreases again.

Compared with TAED and SORMAN, the availability of the acetyl groups in partially acetylated inulin is substantially higher and therefore if the degree of acetylation is sufficiently high the peracetate formation per kg approaches that of TAED. The high availability of acetyl groups in the partially acetylated inulin appears to be a unique property of this inulin derivative. Figure 1 shows a plot of the number of mols of peracetic acid per kg product against the DS_{acetyl}.

Example 1: *Acetylation of inulin, DS 1.0*

50 ml water was added to 30 g inulin (185 mmol, chicory, DP ≈10), after which the mixture was homogenised and adjusted to pH 8 with 2M NaOH. 28 ml (296 mmol) acetic anhydride was added dropwise to the mixture at room temperature whilst the pH was kept at 8 using a pH-stat with the addition of 10M NaOH solution. The temperature was kept at 25 °C. 15 minutes after all the acetic anhydride had been added, the solution was diluted with water to a volume of approximately 500 ml and the pH was adjusted to 6. After standing overnight the precipitate was filtered off. The filtrate was purified by nanofiltration. The filtrate from the nanofiltration was concentrated (Rotavapor) and the residue was dried in a vacuum oven at 70 °C. Yield: 36.25 g (95%) with a DS (degree of substitution) in acetyl of 1.01. Reaction efficiency: 63%. The product had a surface tension (1% g/g solution at 30 °C) of 47.78 ± 0.06 mN/m. The product released an amount of peracetate (in mol%, determined in accordance with the procedure as described in Example 9) of 74 mol% or 3.7 mol peracetate per kg product.

Example 2: *Acetylation of inulin, DS 0.5*

Example 1 was repeated, but using 15 ml (159 mmol) acetic anhydride. DS: 0.51; yield: 98%; reaction efficiency: 73%.

Example 3: *Acetylation of inulin, DS 1.5*

Example 1 was repeated, but using 58 ml (613 mmol) acetic anhydride. DS: 1.51; yield: 84%; reaction efficiency: 53%.

Example 4: *Acetylation of carboxymethylinulin*

218 g acetic anhydride was added dropwise to a solution of 150 g carboxymethylinulin (CMI, DS 0.88) in the course of 3 hours whilst the pH was kept at 8 using 10M NaOH and the temperature was kept at 25 °C. 15 minutes after all the acetic anhydride had been added the solution was diluted with water to a volume of approximately 2.3 l and the pH was adjusted to 6. After standing overnight the precipitate was filtered off. The filtrate was purified by electrodialysis. The product was concentrated (Rotavapor) and the residue was dried in a vacuum oven at 70 °C. Yield: 134.6 g (74%) with a DS (degree of substitution) in acetyl of 1.2. Reaction efficiency: 63%.

Example 5: *Acetylation of inulin with NaOAc in acetic anhydride at 140 °C*

A suspension of inulin (30 g) and sodium acetate (3 g) in acetic anhydride (150 ml) was heated (140 °C, 4 hours). The hot reaction mixture was poured into ice-water (approximately 2 l) and stirred overnight. The resulting precipitate was filtered off and dried in air. Yield: 47.2 g (89%). DS_{acetyl}: 3.0. Reaction efficiency: 38%.

Comparative Example A: *Acetylation of carboxymethylinulin in an acid medium*

A mixture of acetic anhydride (25 ml) and acetic acid (10 ml, 100%) was added dropwise to a solution of CMI (DS 1.0; 10 g) in acetic acid (50 ml, 100%) and concentrated sulphuric acid (0.3 ml) and the mixture was then stirred (3 hours, 50 °C). The solution was cooled and filtered through a glass filter. The residue was washed (400 ml acetone/water (3:1)). After removing acetone from the combined filtrates (Rotavapor) the product was desalinated by means of nanofiltration. The residue was freeze-dried. Yield: 5.8 g (53%). DS_{acetyl}: 0.49. Reaction efficiency: 8%.

Comparative Example B: *Acetylation of CMI DS 1.0 with NaOAc and acetic anhydride at 120 °C*

A suspension of CMI (10 g, DS 1.0) and sodium acetate (0.5 g) in acetic anhydride (50 ml) was heated (120 °C, 4 hours). After cooling to room temperature the precipitate was removed by means of filtration and the residue was washed with acetic anhydride. The filtrate was concentrated under vacuum (Rotavapor). The residue was then taken up in water and freeze-dried. Yield: 7.7 g (68%). DS_{acetyl}: 0.78. Reaction efficiency: 7%.

Comparative Example C: *Acetylation of CMI (DS 1.0) with NaOAc in acetic anhydride at 140 °C*

Example 5 was carried out using CMI (10 g, DS 1.0), sodium acetate (0.5 g) and acetic anhydride (50 ml). Yield: 27.7 g (73%). DS_{acetyl}: 1.5. Reaction efficiency: 13%.

Example 6: *Propionylation of inulin*

50 ml water was added to 30 g inulin (185 mmol, chicory, DP ≈ 10), after which the mixture was homogenised and the pH was adjusted to 8 with 10M NaOH. 50 ml (388 mmol) propionic anhydride was added dropwise to the mixture at room temperature whilst the pH was kept at 8 and the temperature was kept at 25 °C. After standing overnight the precipitate was separated off, rinsed with water and filtered off. The residue was dried in air. Yield 41.0 g (92%) with a DS (degree of substitution) in propionyl of 1.41. Reaction efficiency: 67%.

Comparative Example D: *Reproduction of Example 14 in EP-A 792 888*

15 g (0.09 mol) inulin was dissolved in 250 ml water. 12.3 ml (0.09 mol) propionic anhydride and 300 g Merck III ion exchanger (OH^- form) were added to this solution. The mixture was heated for 24 hours at 40 °C with stirring. The solution was filtered (Büchner) and the filtrate was evaporated. After adding 100 ml water, the mixture was filtered again. The filtrate was freeze-dried. The yield was so low (158 mg) that characterisation was dispensed with. Various attempts to improve the result (a: repetition; b: extract resin with water, evaporate extract as well; c: rinse resin with methanol, evaporate methanol fraction as well; d: lower pH from 11 to 6 after reaction) gave no improvement.

Example 7: *Bleach activator test procedure*

Mix the following solutions:

- 15 ml 0.6% hydrogen peroxide solution
- 10 ml saturated sodium pyrophosphate solution
- 10 ml 0.05% EDTA solution.
- Make up to 100 ml with demineralised water and heat to 30 °C.
- Add the heated mixture to an accurately weighed amount (75 - 90 mg) of bleach activator in a 600 ml glass beaker.
- Adjust the pH to 11.6 with 0.1 M NaOH solution.
- Precisely 4 minutes after the first addition add 30 ml 0.1% catalase solution.
- Adjust the pH to 10.5 with 0.5 M sulphuric acid solution and cool the solution to 0 - 3 °C.
- Precisely 6 minutes after the first addition add 15 ml 100% acetic acid solution and 15 ml 10% potassium iodide solution.
- Titrate the liberated iodine against a 0.1 M thiosulphate solution.

The mol% peracetic acid liberated from the bleach activator can be calculated from the quantity of thiosulphate solution required, 2 mmol thiosulphate corresponding to 1 mmol peracetic acid formed. The determinations were corrected for the loss of peracetic acid during the measurement. The correction factor for this loss is 1.10. The results of these determinations are given in Table 1.

Claims

1. Use of a partially acylated fructan having a degree of substitution with acyl groups of 0.4 - 2.5 and a degree of substitution of less than 0.5 with other substituents as a bleach activator.

2. Use according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

3. Use according to Claim 1 or 2, wherein the fructan is acylated with a degree of substitution of 0.6 - 1.8.

4. Use according to one of Claims 1 - 3, wherein the fructan has an average chain length of 3 - 60, in particular 4 - 30.

5. Use according to one of Claims 1 - 4, wherein the degree of substitution of carboxymethyl groups is less than 0.2.

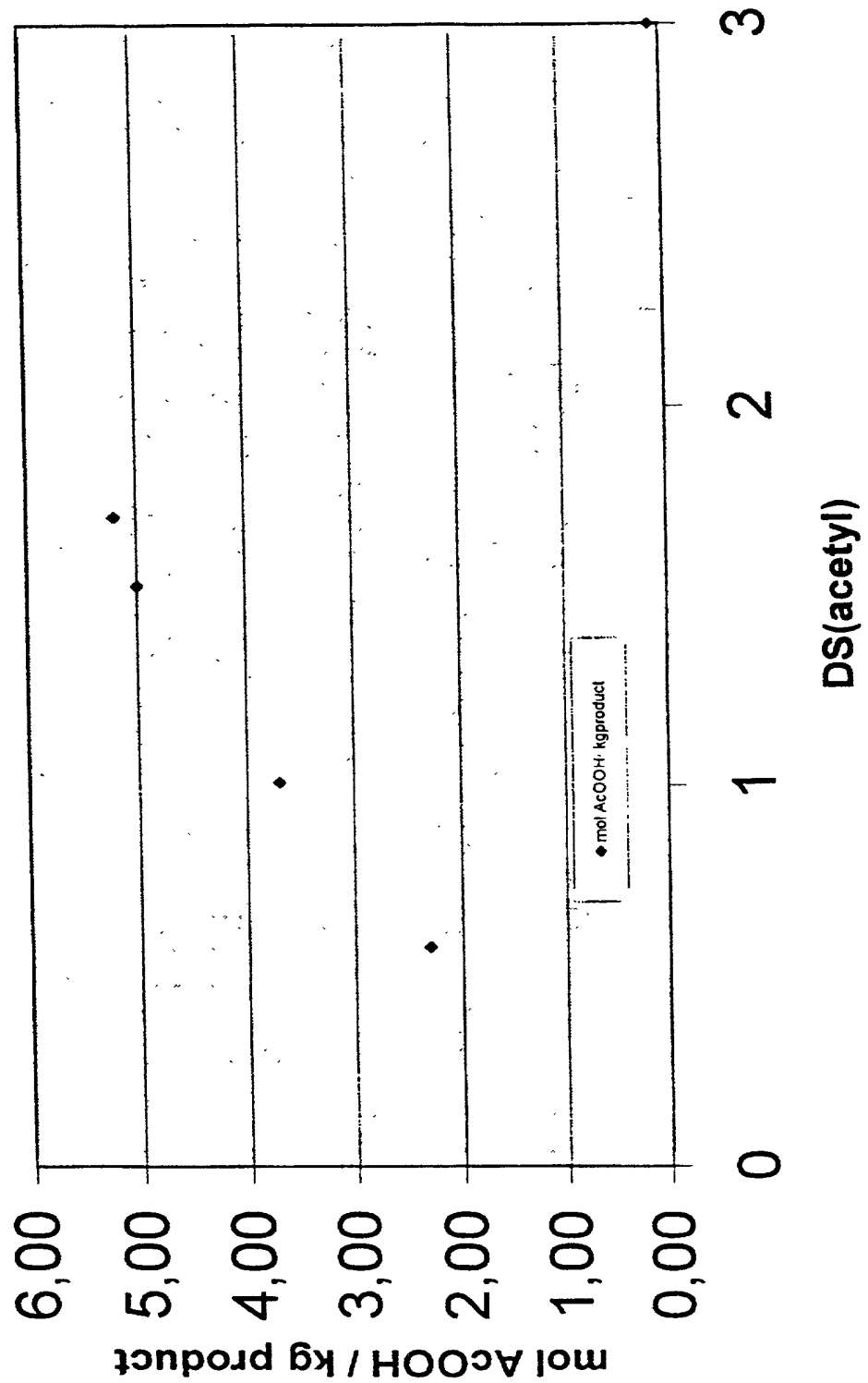
6. Use according to one of Claims 1 - 5, wherein the fructan is inulin.

7. Use according to one of Claims 1 - 6, wherein the fructan is acylated with acetyl and/or propionyl groups.

8. A process of producing an acetylated and/or propionylated fructan or fructan derivative by acylation of the fructan or derivative thereof with a reactive acyl derivative of acetic and/or propionic acid, characterised in that the acylation is carried out in an aqueous medium at a pH of between 7 and 9.

9. A process according to Claim 8, characterised in that the acylation is carried out at a temperature of between 0 and 40 °C.

10. Partially acetylated and/or propionylated fructan obtainable using the method according to Claim 8 or 9, which has a solubility in water of at least 1 g/l, in particular of at least 2 g/l.


mol AcOOH / kg product
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0
1
2
3
DS(acetyl)
mol AcOOH· kgproduct

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL DESIGN, NATIONAL STAGE OF PCT OR CIP APPLICATION)

As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Bleach Activator based on Inulin

the specification of which: (complete (a), (b) or (c) for type of application)

REGULAR OR DESIGN APPLICATION

a. [ ] is attached hereto.

b. [ ] was filed on as Application
Serial No. and was amended on
(if applicable)

PCT FILED APPLICATION ENTERING NATIONAL STAGE

c. [X] was described and claimed in International application No. PCT/NL00/00462
filed on 30 June 2000
and as amended on (if any)

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, paragraph 1.56(a).

In compliance with this duty there is attached an information
disclosure statement 37 CFR 1.97

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35. United States Code paragraph 119 of any foreign application (s) for patent of inventor's certificate listed below and have also identified below any foreign application for patent of inventor's certificate having a filing date before that of the application on which priority is claimed.

(complete (d) or (e))

d. [ ] no such applications have been filed
e. [X] such applications have been filed as follows

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION

Country	Application Number	Date of filing (day, month, year)	Date of Issue (day, month, year)	Priority claimed
The Netherlands	1012482	30 June 1999		Yes

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION

_____

_____

CONTINUATION-IN-PART

(Complete this part only if this is a continuation-in-part application)

I hereby declare claim the benefit under Title 35, United States code, paragraph 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claim of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, paragraph 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, paragraph 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Filing date) (Status) (patented, pending, abandoned)

(Application Serial No.) (Filing date) (Status) (patented, pending, abandoned)

POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoît CASTEL, Reg. No. 35,041, Eric Jensen, Reg. No. 37,855, and Thomas W. PERKINS, Reg. No. 33,027 and Roland E. Long, Jr. Reg. No. 41,949 c/o YOUNG & THOMPSON, Second Floor, 745 South 23rd Street, Arlington, Virginia 22202.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

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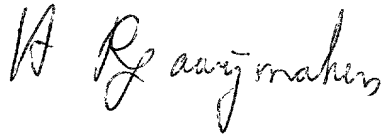

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